

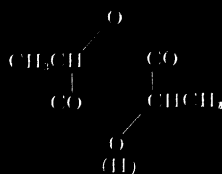
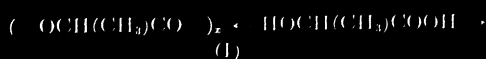
Lactic Acid Condensation Polymers

PREPARATION BY BATCH AND CONTINUOUS METHODS

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CONDENSATION products or polymers of lactic acid are important because: (a) They occur in all aqueous solutions of lactic acid containing approximately 18% lactic acid or more. (b) They are promising chemical intermediates. (c) The condensation polymers of intermediate molecular weight can be used as such or after slight alteration as plasticizers. (d) The condensation products of higher molecular weight can be converted into useful plastics by condensation with certain vegetable oils, glycols, and other chemicals. (e) They are excellent for storing and transporting lactic acid in a highly concentrated condition; the completely polymerized linear product (I) and lactide (II) are equivalent to 125% lactic acid:

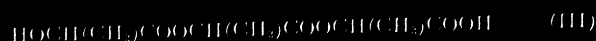


Our interest in the production and properties of polymerized lactic acid was created largely by finding that the linear condensation polymers constitute an excellent starting point for making methyl lactate (19). When methyl lactate is formed by the interaction of polylactic acid and methanol, probably alcoholysis as well as esterification is involved, and only small quantities of water are formed in the reaction. Absence of water is advantageous because methyl lactate is readily hydrolyzed during distillation when appreciable quantities of water are present. Moreover, methyl lactate and water distill as an azeotropic mixture. The present paper summarizes earlier information on polylactic acid, much of which (3, 6) has not been readily available and describes both batch and continuous methods for dehydrating or polymerizing lactic acid.

The preparation, properties, and reactions of condensation polymers of lactic acid are reviewed; batch and continuous methods for converting lactic acid into its condensation polymers are described. Removal of water during the dehydration or self-esterification of lactic acid is facilitated by relatively high temperatures, reduced pressure, sulfuric acid or similar esterification catalyst, and an entraining agent, such as benzene or toluene. The resulting condensation polymers, which react readily with methanol, are useful for making methyl lactate.

PREVIOUS INVESTIGATIONS

Although the reported findings of previous workers are not in complete agreement, aqueous lactic acid solution and dehydrated lactic acid appear to consist mainly of "free lactic acid" (monomeric α -hydroxypropionic acid), water, and linear condensation or self-esterification products, such as lactyl lactic acid and lactyl lactyl lactic acid, III:



The three components, occurring in various proportions, the extreme limit being pure water and completely polymerized lactic acid, I, lactide, II, have the same ultimate composition as completely polymerized lactic acid, but appear to occur only in traces (3, 6, 12, 13, 16, 17) in equilibrium mixtures of monomeric lactic acid, water, and polylactic acid. The case (I, 6, 26, 30) with which lactide, II, is hydrolyzed to lactyl lactic acid is of interest in this connection.

The composition of various equilibrium mixtures of monomeric lactic acid, water, and polylactic acid is shown in Figure 1, prepared from data taken from publication of Bezzi, Riccoboni, and Sullam (6), Watson (70), and Thurmond and Edgar (39). The linear condensation polymer was considered as one component in the preparation of Figure 1, although the polymers were principally lactyl lactic acid (the dimer) in the relatively dilute solutions and higher polymers (such as di-, tri-, and tetralactyl lactic acid) in the more concentrated solutions (6). The variation in molecular weight of the polylactic acid with concentration (6) expressed as total acidity after hydrolysis is shown in Figure 2. Other workers assumed that the polylactic acid occurring in lactic acid solutions was the dimer, lactyl lactic acid. Other data regarding the composition of equilibrium mixtures of lactic acid are given in Table I.

Figures 1 and 3 show that both water and polylactic acid can occur in concentration as high as 100%, but that the highest concentration reached by monomeric lactic acid in equilibrium mixture is 47 mole % or 62% by weight. The highest mole and weight concentrations of monomeric acid are attained when the total acidity after hydrolysis is 100, 135 and 80%, respectively. Instead of having the usual connotation of purity, "100% concentration" when applied to lactic acid designates a mixture containing approximately 47 mole % monomeric lactic acid, 34 mole % water, and 19 mole % polylactic acid; the polylactic acid has an average degree of polymerization (6) of 2.75. Water, an important constituent of "100% lactic acid", occurs in ap-

TABLE I. COMPOSITION OF EQUILIBRIUM MIXTURES OF LACTIC ACID

Total Acidity (after Hydrolysis), % as Monomeric Lactic Acid	Alkanoic acid	Poly lactic acid	Water	Sp. Gr.	Clara Gram
102.43	39.75	62.48		1.1869	(16)
91.41	37.97	53.49	8.59	1.2036	(16)
81.88	62.77	19.61	1	1.1603	(16)
80	62	18	20		(16)
50	16.5	3.5	80		(16)
51.93	19.14	0.79	18.07	1.1107	(16)
30	19.6	0.1	80		(16)
100	29.6	26.9	3.5		(17)
90	59.98	30.62	10.1		(17)
Syrupy acid	50	30	10		(16)
90	60	30	10		(17)

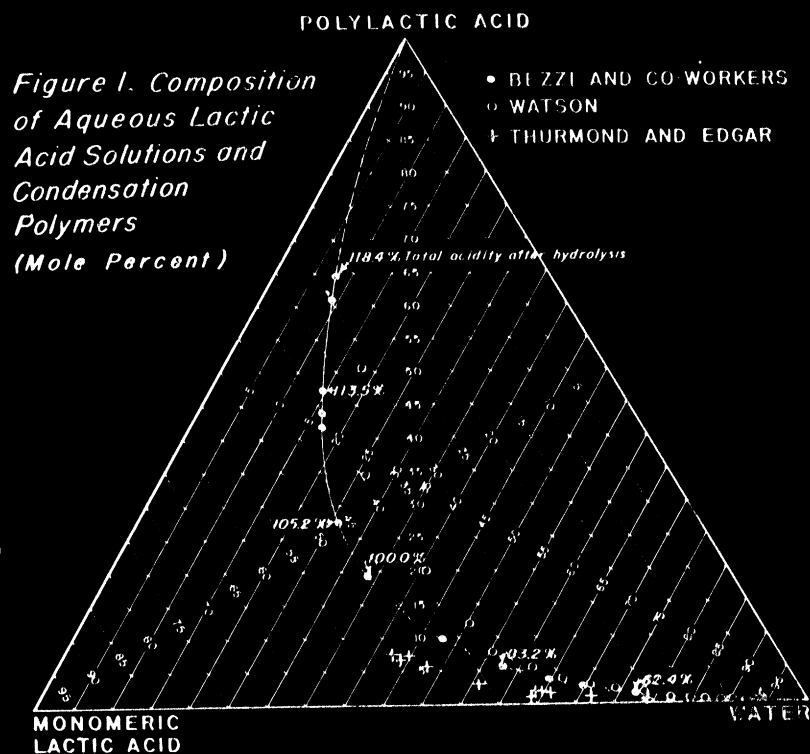


Figure 1. Composition of Aqueous Lactic Acid Solutions and Condensation Polymers (Mole Percent)

preciable quantities even in the condensation polymers of lactic acid (Figure 1).

It should be noted in passing that relatively pure monomeric lactic acid can be obtained by evaporation of dilute lactic acid at low temperature (29) and by suitable distillation (6) of lactic acid (which includes collection of the product at low temperature). Lactide, 11, can be prepared conveniently by the distillation of polylactic acid under reduced pressure (4, 5, 9, 12).

Eder and Kutter (16) studied the effect of temperature upon the equilibrium in 50% lactic acid and concluded that temperature has a negligible effect upon the equilibrium finally reached between room temperature and 98° C. Temperature has a profound effect, however, upon the rate at which the equilibrium is attained. When 100% lactic acid was diluted to 50%, approximately 100 days at room temperature or 12 hours at 98° C. were required to bring the solution to equilibrium. The presence of mineral acid hastened the attainment of equilibrium (46).

As would be expected from the fact that the formation of polylactic acid is essentially self esterification, the conversion of lactic acid into its polymers has always been effected by removing water. Removal of water, including free water and that formed in esterification, has been accelerated by relatively high temperatures (37, 42), reduced pressures (27, 28, 31, 34), and entraining agents (40, 42) such as air (34), toluene, and ethylene chloride. Since polylactic acid is produced by esterification, it seems odd that esterification catalysts, such as sulfuric acid, have not been generally used.

Data obtained by Hovey and Hodgins (35) at 210° C. and by Bezzi and co workers (6) at 120° are plotted in Figure 4. Dehydration was 50% complete (that is, 1 mole of water was removed for each 2 moles of lactic acid) in approximately 30 minutes at 210° C.; nearly 9 hours were required for 50% dehydration at 120° C. Bezzi's data approximated a straight line when the degree of dehydration was plotted against the reciprocal of time. By extrapolating the reciprocal of time to zero, it was estimated that lactic acid can be 94% dehydrated by heating at 120° for an infinite period.

TABLE II. PREPARATION OF LACTIC ACID CONDENSATION POLYMERS (BATCH METHOD)

Exptl. No.	Grams	Lactic Acid %	Moles	Temp., °C.	Pressure, Atm.	Catalyst	Entraining Agent, ml.	Time, Hr.	Polylactic Acid (Residue)					
									Distillate, G.	Dehy. dila tion, % ^a	Equivalent wt. Tota tion ^b	Calcu lated ^c	Mol. Wt. d	Grams
1	1121	80.3	10	100	150	25.30	None		312	67	79.2	77.9	198	
2	1300		11.6	100	150	30.34	None		414	76	77	76.3	277	5
3	1121		10	100	150	25.30	None		340	66	78.1	78.1	330	
4	2309		20.6	100	150	25.30	None		761	83	76.5	75.1	306	
5	512		4.57	100	150	20.70	Toluene-sulfonic acid, 5 g.		179	95	73.7	72.9	1458*	2.2
6	512		4.57	100		17	H ₂ SO ₄ , 5 ml.		167	80	76	75.6	342	2.4
7	908		8.1	130		25	H ₂ SO ₄ , 8 ml.		267	81			397*	
8	554	81.3	5			Atm.	H ₂ SO ₄ , 5 ml.	Benzene, 200	191	97			2418*	
9	220	81.7	2	115		Atm.	None		10					
10				115		Atm.	H ₂ SO ₄ , 1 ml.		6					
11				115		37.40	None		6.2	71	8.4	65		
12				115		37.40	H ₂ SO ₄ , 1 ml.		6.2	79	7.6	90		
13				135		Atm.	None		8.1	41	1.2	0		
14				135		Atm.	H ₂ SO ₄ , 1 ml.		8.1	42	1.3	1		
15				135		38	None		3.33	90	22.5	86		
16				135		38	H ₂ SO ₄ , 1 ml.		3.33	82	9.9	94		
17				85	103	Atm.	None	Benzene, 100	32.2	71	1.4	82		
18				85	96	Atm.	H ₂ SO ₄ , 1 ml.		10.9	78	0.7	105		
19				86	115	Atm.	H ₂ SO ₄ , 2 g.	Benzene, 100	18.2	76	0.7	93		
20				104	120	Atm.	None	Toluene, 100	19.8	73		108		
21				102	155	Atm.	H ₂ SO ₄ , 1 ml.		6.25	79		93		
22				108	145	Atm.	None	Xylene, 100	3.42	70		82		
23				108	145	Atm.	H ₂ SO ₄ , 1 ml.		1.42	71		75		

^a Calculated on basis of water removed (100% dehydration represents distillation of all free water, 1.1 mole water per mole lactic acid).

^b Ultimate neutralizing capacity expressed as grams polylactic acid capable of reacting with 40 grams NaOH (calculated from total amount of standard NaOH solution required to neutralize and assuming a known quantity of sample).

^c Calculated by the formula: Equivalent weight = $\frac{100}{\% \text{ dehydration}} \times 1.90$.

^d Calculated from equivalent weight determined by titration and hydrolysis.

* Calculated by formula: Mol. wt. = $\frac{72}{100 - \% \text{ dehydration}} \times 1.90$.

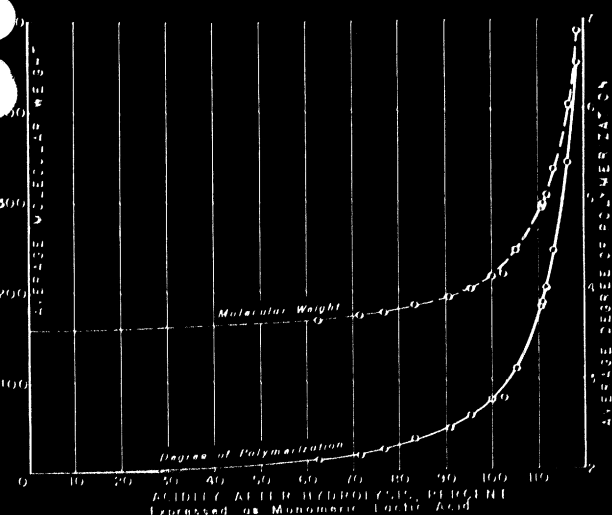


Figure 2. Average Molecular Weight of Lactic Acid Polymers

The effect of temperature on the rate of dehydration or self esterification is illustrated by the following data (*b*, *25*):

Temp., °C.	Time, Hr.	Degree of Polymerization
80	93	2.71
120	93	11.30
120	7	1.7
150	7	3.06

An increase in temperature from 80° to 120° C. raised the degree of polymerization in 93 hours from 2.71 to 11.30; increasing the temperature from 120° to 150° C. raised the degree of polymerization in 7 hours from 1.7 to 3.06. Lactic acid has been dehydrated at 70° under reduced pressure (25) and at room temperature in a desiccator (*4b*) containing sulfuric acid over periods of 2 to 18 months.

Lactic acid polymer (*14*) of relatively high molecular weight (approximately 3000) can be made conveniently by heating lactide, II, at 150° to 250° C. According to Bezzi and co-workers (*6*), a trace of water is required for this transformation. Poly(lactic acid) with an average degree of polymerization of about 60 and a molecular weight of approximately 4300 has been prepared (*6*) from lactide, II. Bezzi and co-workers (*6*) stated that the preparation of poly(lactic acid) having a molecular weight higher than 5000 is unlikely, owing to production of water by decomposition reactions which accompany the polymerization of lactide.

The properties of poly(lactic acid) are affected profoundly by the molecular weight. Solubility in organic solvents (*12*), such as ether, benzene, and carbon tetrachloride, and viscosity increase with increase in molecular weight, whereas solubility in water decreases (*6*). The dimer and higher polymers are relatively strong acids and have dissociation constants (*6*) approximately five times the constant of monomeric lactic acid when dissolved in water or water-alcohol solutions. According to Bezzi, the viscosity behavior (*3*) of poly(lactic acid) solutions is to be explained by the size and shape of the molecule rather than by solvation. The polymer of moderate molecular weight are viscous oils, whereas those having molecular weights of approximately 3000 and above are brittle, glass-like materials (*4, 5*).

Lactyl lactic acid, which can be prepared (*6*) conveniently by the hydrolysis of lactide, II, is a highly viscous oil (*12*). Poly(lactyl) (*15*) of the dimer at 20° C. in the absence of a catalyst is slow. Lactyl lactic acid (*17*) has been obtained, admixed with lactide, by distilling lactic acid. The trimer (melting point 39° C., boiling point 235–40° under 20 mm. pressure) was separated from lactide by extraction with ether. It was found to be soluble in ether, chloroform, benzene, and acetic acid. The trimer was hygroscopic and decomposed when distilled at atmospheric pressure. Monomeric lactic acid (*6, 31*) (dextro or levo) melts at 52.8°. Optically inactive lactic acid (*6*), which melts at 16.8° C., has been distilled under the following conditions: 32–5° C. under 0.5–1 mm. and 122° under 11–15 mm. pressure.

When distilled (*9, 12, 21, 24, 30*), preferably in a vacuum and at a high rate, poly(lactic acid) are converted into lactide, II. Bezzi and co-workers (*6*) claim that the dimer and trimer, but not the higher polymers, are converted into lactide by this treat-

ment. According to Engelhardt (*43*), poly(lactic acid) is stable at temperatures up to 250° C. When heated at 250° to 260°, poly(lactic acid) decomposes (*33*) into carbon monoxide (chief gaseous constituent), carbon dioxide, acetaldehyde, lactide, citraconic acid, aqueous lactic acid, and 1 or 2% of carbonyl compound. When lactide is heated to 250° C., it decomposes (*43*) into the same products obtained by the pyrolysis of poly(lactic acid).

Several workers (*34*) have fractionated poly(lactic acid) with solvents. Bezzi (*6*) fractionated the polymer by adding water or petroleum ether to an acetone solution. Watson (*43*) added petroleum or terpene hydrocarbons to acetone or benzene solutions of poly(lactic acid).

Poly(lactic acid) behaves as an ester when treated with water and alcohol. Hydrolysis (*42, 46, 46a*) of the polymer in the presence of a catalyst at elevated temperatures is rapid. Methyl (*4, 23*), ethyl (*9, 10*), isopropyl (*9, 10*), amyl (*10*), glyceryl (*10*), allyl (*40*), and benzyl (*43*) lactates have been prepared by treating poly(lactic acid) with the appropriate alcohol. Wilhelm (*44*) prepared lactamide and ammonium lactate by treating poly(lactic acid) with ammonia.

The alcohol and carbonyl groups present in poly(lactic acid) have been used to prepare a non-flammable plastic. It is claimed that useful plastics can be made by treating poly(lactic acid) with alcohols (*15*), acids (*11*), and aldehydes (*41*), aldehydes (*41*), and carbohydrazide (*41*). Light (*43*) reviewed the preparation of plastics (*35*) from lactic acid (*32*).

BATCH DEHYDRATION OF LACTIC ACID

Approximately 30% aqueous solution of lactic acid (total acidity after hydrolysis) were concentrated into lactic acid polymers by both batch and continuous methods. On the basis of work by Bezzi (*6*) and others, it was assumed that the dehydration products consisted almost entirely of linear polymer and that lactide was present only in traces.

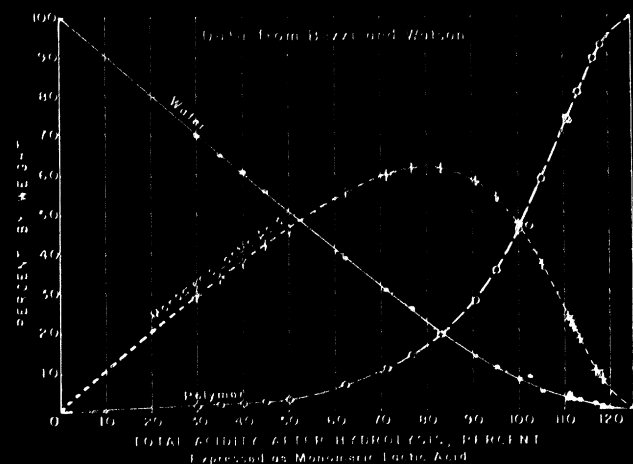


Figure 3. Composition of Aqueous Lactic Acid Solutions and Dehydrated Lactic Acid

When lactic acid was dehydrated discontinuously, water was distilled from the 30% lactic acid (almost colorless, edible grade) under various pressures and at temperatures ranging from 85° to 150° C. (Table II). Entraining agents and esterification catalysts were used in some of the experiments. Equivalent and molecular weights (Table II) were estimated from the amount of standard alkali required to neutralize and saponify known quantities of poly(lactic acid). Since the amount of sulfuric acid remaining unchanged in the product was not known, the titration data were not corrected for the catalyst used. Polymers of high molecular weight (experiments 3, 13, and 19) were obtained by removing the water with an entraining agent in the presence of a mineral acid catalyst. The poly(lactic acid) obtained in experiment 3, 13, and 19 were firm brown solids. The samples obtained with boric acid were lighter in color than those with sulfuric acid as catalyst. Possibly a boric acid-lactic acid complex with the catalyst when boric acid was added to the mixture.

Lactic acid was dehydrated in several experiments to determine the effect of temperature, time, pressure, and catalyst (Table II and Figure 5). The lactic acid sample and the neck of the flask leading to the condenser were heated by vapors of boiling *n*-butanol or *n*-pentanol. The fact that a distillation column was not used is partly responsible for distillation of lactic acid along with the water.

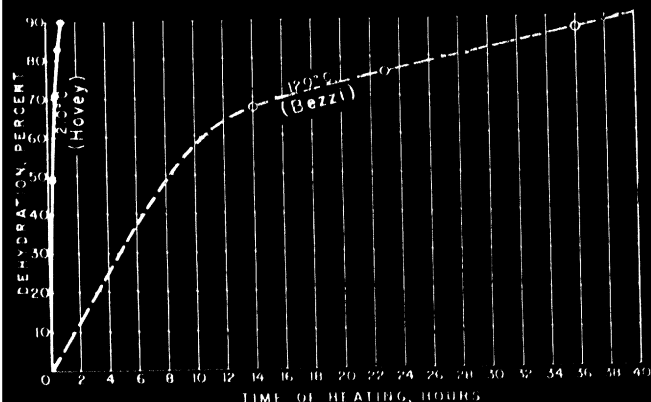


Figure 4. Dehydration of Lactic Acid at 120° and 210° C.

When lactic acid was dehydrated at 115° C. under atmospheric pressure, the presence of sulfuric acid did not accelerate the distillation of water (Figure 5). Dehydration at 115° under atmospheric pressure was so slow that complete dehydration (removal of one mole of water per mole of lactic acid) would not have been reached in any reasonable time. Use of reduced pressure accelerated dehydration to a remarkable degree. For example, 70 ml. of water were removed under 37 to 40 mm. pressure in 6 hours, whereas only 8 ml. of water were removed in the same time at atmospheric pressure.

Although sulfuric acid was not beneficial when 81.7% lactic acid was dehydrated at 115° C. under atmospheric pressure (1 ml. of concentrated acid in 2 moles of 81.7% lactic acid), the sulfuric acid accelerated the removal of water at 115° under reduced pressure (Figure 5). The amount of distillate obtained in 1 hour in the absence and in presence of sulfuric acid, respectively, were 55 and 74 ml.

For the dehydration experiments at 135° C. (Figure 5), the reaction mixture and the neck of the flask were heated by the vapors of boiling *n*-pentanol. Two moles of 81.7% lactic acid were dehydrated, and the results are roughly similar to those obtained at 115° C. Sulfuric acid had little effect upon the rate of dehydration under atmospheric pressure. After 8 hours at 135° C., 41–42 ml. of distillate were collected, both in the presence and in absence of sulfuric acid. The influence of reduced pressure was considerable (Figure 5) but not so pronounced as at 115°. The data

indicate that sulfuric acid has an accelerating effect for the first hour under reduced pressure, after which the rate of dehydration decreases. At 135° C. under reduced pressure, after the first hour the rate of dehydration was greater in the absence of sulfuric acid than in its presence.

Figure 5 shows that an increase in temperature had a marked influence upon dehydration under atmospheric pressure. The distillates collected after 1 hour at 115° and 135° C., respectively, were 3 and 32 ml.

In agreement with previous workers, entraining agents facilitated the removal of water from lactic acid under atmospheric pressure. Only 3 ml. of distillate were obtained in 1 hour at 115° C. (Figure 5) in the absence of an entraining agent, but 35 ml. were collected in 1 hour when benzene was the entraining agent, even though the temperature of the reaction mixture was only 85° to 103° C. Both sulfuric and boric acids increased the rate of dehydration when entraining agents were used (Figure 6).

With entraining agents, the rate of removal of water was proportional to the boiling points of the agent. For example, 48, 51, and 63 ml. of distillate were obtained in 2 hours when benzene, toluene, or xylene, respectively, was the entraining agent (Figure 6). Decomposition was noted with xylene as agent, toward the end of the dehydration when the temperature was approximately 145° C. This result was unexpected, since it has been reported that polylactic acid is stable up to 250°. Table II shows that appreciable amounts of lactic acid may distill under some conditions during dehydration. The quantity of acid which distilled when benzene was the entraining agent was small.

CONTINUOUS PRODUCTION OF POLYLACTIC ACID

Polylactic acid was prepared continuously under reduced pressure by passing approximately 80% lactic acid down a heated column (Pyrex tube, 1 inch in diameter and 4 feet long) packed with small porcelain Berl saddles, by withdrawing water vapor from the top of the column, and by removing lactic acid polymers from the bottom. The tower was heated electrically, and the temperature was controlled and recorded automatically. Although the polymers were viscous semisolids at room temperature, they were rather fluid at about 100° C. and easily withdrawn from the bottom of the tower. Water vapor withdrawn from the top of the tower was condensed and titrated to determine the acid content. It was assumed that the acidity of the distillate was caused by lactic acid. The temperatures listed in Table III were recorded from a thermocouple located 2 feet from the bottom of the column.

Comparison of experiments 216, 217, and 218 with later experiments shows that sulfuric acid in concentrations higher than 0.05

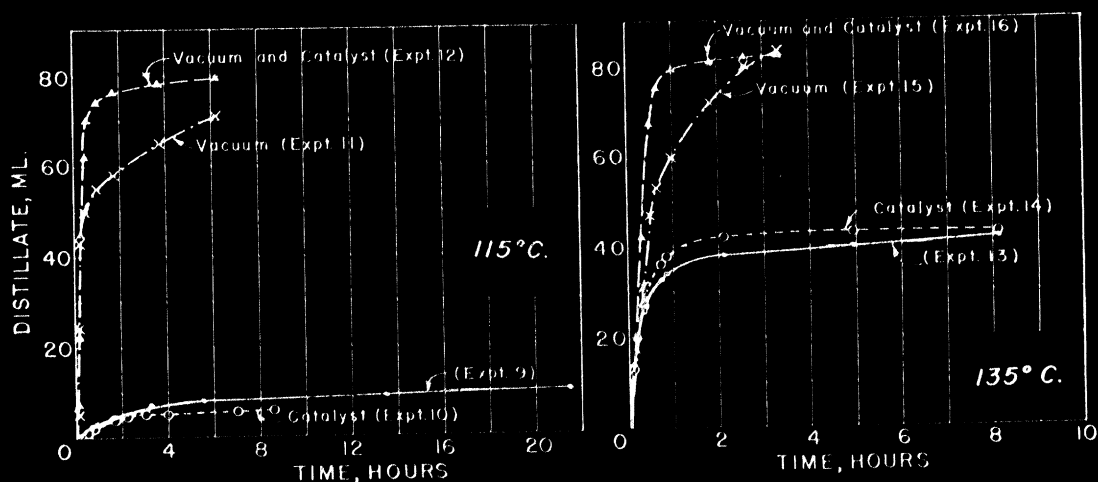


Figure 5. Dehydration of Lactic Acid at 115° and 135° C.

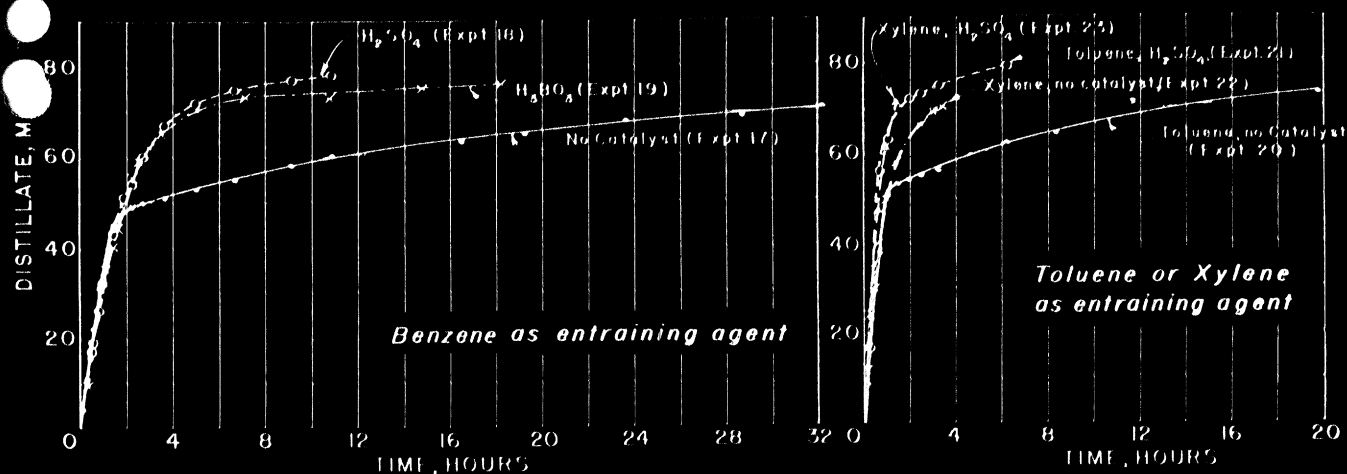


Figure 6. Dehydration of Lactic Acid with Benzene, Toluene, or Xylene as Entraining Agent

ml. per mole of lactic acid was highly effective in facilitating dehydration. Toluene-sulfonic acid also behaved as a catalyst. The effect of the amount of concentrated sulfonic acid can be estimated from Table III; although 0.05 ml. sulfonic acid per mole of lactic acid has little effect, 0.1 ml. sulfonic acid has a pronounced accelerating action. Apparently sulfonic acid concentrations higher than 0.25 ml. per mole of lactic acid are not advantageous. Possibly other conclusions will be reached when lactic acid of higher or lower concentration is used.

Although the agreement is not entirely satisfactory, some of the experiments indicate that removal of water from the lactic acid is favored by increasing the temperature of the tower.

Under some conditions (experiments 272, 273, 279, and 280) considerable quantities of lactic acid distilled. This lactic acid was obtained as a moderately concentrated solution (23 to 44%

by weight) of excellent purity. The maximum quantity of lactic acid obtained in the distillate was 27% of that passed into the tower, but 44% of the lactic acid originally present in the monomeric form (estimated from Figure 3). The colorless lactic acid obtained in the distillate could be used as such for some purposes or recycled and converted into polylactic acid.

Probably further self-esterification of lactic acid took place during dehydration. It is conceivable, however, that the esterification during the earlier stages of the dehydration was negligible under some conditions. On this basis, 45.1 grams of free water (estimated from Figure 3) would be removed from 220 grams of 81.7% lactic acid, leaving a residue (174.9 grams) containing 22% by weight of polymer. The degree of dehydration of the residue obtained in this manner would be 44.2%.

TABLE III. CONTINUOUS DEHYDRATION AND POLYMERIZATION OF LACTIC ACID

Expt. No.	Lactic Acid ^a		Temp., °C.	Time, Hr.	Pressure, Mm.	Catalyst	Distillate, G.			Polylactic Acid		
	Grams	%					Total	Acid content ^b , wt. %	Dehydration, %	Grams	Equivalent wt., %	Loss, Grams
247	224	80.3	119-135	3-66	10	None	55	1.1	37	166	83.0	3
248	224	80.3	135-149	1-5	12		56	3.3	24	132	82.5	364
248	224	80.3	152-172	3-33	10		54	-	-	166	84.0	4
251	221	81.3	121-129	2-33	11	CH ₃ COCH ₂ CO ₂ H, 2 grains	62.7	0.8	57		79.0	
252	221	81.3	122-131	2-75	10		70.8	1.2	79	146	77.0	4
249	224	80.3	143-151	2-5	10		69	1.4	65	146	77.5	9
253	191	81.3	147-152	6-0	10		62.2	1.2	81		76.0	
256	221	81.3	94-106	2-5	11	H ₂ SO ₄ , 2 ml.	67.5	0.9	70	148	76.0	6
254	221	81.3	99-103	3-75	10		67.3	1.0	69	157	74.5	
257	221	81.3	98-106	2-42	9-10		68.8	1.3	73	155	76.8	
255	221	81.3	108-113	2-63	9-10		69.5	2.3	72	152	75.5	0
256	221	81.3	120-125	2-43	9-10		76.2	1.6	93	134	71.6	11
258	221	81.3	131-139	2-77	9-10		72.1	2.3	79	147	75.5	2
259	220	81.7	109-113	2-53	10-11	H ₂ SO ₄ , 1 ml.	73.2	1.1	88	146	75.8	1
260	220	81.7	121-127	3-28	10		74.1	1.6	89	153	74.6	
265	220	81.7	133-140	2-5	5-7		69.6	2.0	76	136	71.7	14
269	220	81.7	135-141	2-13	10		76.1	1.9	94	142	72.5	2
262	220	81.7	103-111	2-27	10	H ₂ SO ₄ , 0.5 ml.	64.2	0.9	64	153	80.0	3
263	220	81.7	116-125	2-52	10		71.8	1.5	83	143	74.5	5
261	220	81.7	123-129	2-20	10		72.9	2.0	85	143	76.2	4
264	220	81.7	130-139	2-17	10		77.1	2.3	96	139	73.5	4
268	220	81.7	146-152	2-30	5-7		73.2	4.5	93	145	72.5	
270	220	81.7	121-129	2-27	10	H ₂ SO ₄ , 0.2 ml.	65.2	1.5	65	154	79.7	1
271	220	81.7	128-133	3-25	10		66.8	2.1	68	147	78.5	
261	220	81.7	141-151	1-55	9-10		68.9	3.8	69	150	77.0	1
278	220	81.7	142-151	2-20	9-10		67.6	3.5	66	154	77.6	
272	220	81.7	143-153	2-00	10-11		93.6	27.1	86	126	75.5	0
279	220	81.7	152-162	2-93	10		111.3	49.1	84	98	74.6	11
280	220	81.7	154-160	2-50	9		82.2	18.7	72	132	75.9	6
273	220	81.7	157-162	2-58	10		85.3	19.8	79	131	76.6	4
282	220	81.7	133-141	3-25, 2-5	10	H ₂ SO ₄ , 0.1 ml.	50.6	1.4	25	168	84.3	2
284	220	81.7	143-152	2-58	9-15		54.2	3.6	29	170	83.4	
290	550	81.7	120-125	5-5	10-37	H ₂ SO ₄ , 1.25 ml.	178.3	19.0	68	320	77.0	524

^a Two mole lactic acid used except in experiments 253 and 250, where 1.73 and 5.0 moles, respectively, were dehydrated.

^b Assumed to be monomeric lactic acid and determined by titration.

^c Ultimate neutralizing capacity expressed in grams capable of reacting with 40 grams NaOH (calculated from total amount of standard NaOH solution required to neutralize and evaporate a known quantity of sample).

^d High loss was due largely to failure to remove all polymer from the reaction tower.

TABLE IV. CONTINUOUS DEHYDRATION OF LACTIC ACID WITH ENTRAINING AGENT IN A PACKED TOWER^a

Expt. No.	H ₂ SO ₄ , ml.	Entraining Agent	Pressure, Atm.	Temp., °C.	Time, Hr.	Dehydration, % ^b
371	1.0	Benzene	Atm.	96-108	4.5	92
372	0.5	Benzene	Atm.	96-108	6.0	87
375	0.25	Benzene	Atm.	87-111	4.3	83
377 ^c	None	Benzene	Atm.	94-130	15.0	72
380	0.25	Toluene	100-140	77-106	3.5	—

^a In each experiment 110 grams 81.7% lactic acid and 200 ml. entraining agent were used. With the exception of experiment 377, approximately 0.5% lactic acid was found in the distillate.

^b Removal of all free water and 1 mole water per mole lactic acid constitutes 100% dehydration. ^c Correction was made for lactic acid in distillate.

^c Approximately 1% of lactic acid distilled.

Lactic acid can be dehydrated or polymerized conveniently also under atmospheric pressure with an entraining agent (Table IV). Lactic acid (81.7%) was passed continuously into the top of the electrically heated packed tower (1 inch in diameter, 4 feet long), benzene or toluene vapor was introduced near the bottom of the tower, and polylactic acid was withdrawn at the bottom. When used as catalyst, sulfuric acid was dissolved in the lactic acid prior to passage into the tower. The vapors (consisting of entraining agent, water, and small amounts of lactic acid) withdrawn from the top of the tower were condensed, the upper layer of the condensate was passed into a heated flask, and the entraining agent was returned as vapor to the bottom of the column. This continuous method of dehydrating lactic acid, which requires neither reduced pressures nor high temperatures, was convenient and easily operated. The resulting polymers contained some benzene or toluene, but their presence should not be objectionable for certain purposes. The entraining agent can be removed from the polymer when its presence is undesirable.

The effectiveness of sulfuric acid as a catalyst was again demonstrated by the experiments of Table IV. When sulfuric acid was not present (experiment 377), the dehydration was only 72%, even though the reaction time was approximately three times that in the other experiments.

Entraining agents might be used in the large scale dehydration of lactic acid to facilitate the removal of water and introduce some of the energy required for dehydration and distillation. Considerable energy could be introduced into the dehydration apparatus by preheating both the entraining agent and the lactic acid to relatively high temperatures (under increased pressure if desirable) just prior to passage into the tower. The use of gases rather than organic liquids would have certain advantages, such as low cost and ease of separation from polymer and distillate.

Although the experiments reported here demonstrate that 80% lactic acid of good quality can be dehydrated conveniently and continuously, it is not claimed that the methods described would prove more economical than dehydration in standard equipment, such as multiple-effect evaporators, now widely used for drying and dehydrating other materials. Crude lactic acid was observed to be less suitable for conversion into the condensation polymers.

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